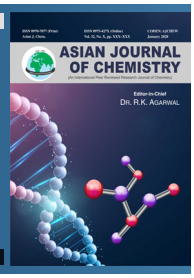
Asian Journal of Chemistry; Vol. 32, No. 8 (2020), 1869-1873

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22636




# Influence of Different Carriers in Polymer Inclusion Membranes for Desalination of Seawater

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*Received*: 14 January 2020; *Accepted*: 5 April 2020; *Published online*: 27 July 2020; AJC-19960

Desalination of seawater using various polymer inclusion membranes was carried out. Polymer inclusion membrane (PIM) is known to have the highest stability, able to overcome liquid membrane instability and was placed in between two phases: the source phase is seawater and the receiving phase is the micro-filtered water. Determination of salinity levels in the feed phase and the receiving phase was carried out using a salinity meter, while membrane characterization was done using FTIR and SEM techniques. Polyvinyl chloride (PVC) based PIM membranes were prepared using different single and mixed synergtic carriers ratio of 1:1 *viz*. dibutyl ether, methyl-trioctylammonium chloride (Aliquat 336), di-(2-ethylhexyl)-phosphate (D2EHPA), thenoyl trifluoroacetone (HTTA), tributyl phosphate (TBP) and eugenol (PE). The results showed the salinity value for single HTTA carriers had a greater salinity value in comparison to mixed carriers (HTTA:TBP; HTTA:Aliquat; D2EHPA:TBP; and D2EHPA:Aliquat) gave different salinity value towards the desalination process.

**Keywords: Polymer inclusion membrane, Salinity, Desalination.**

## INTRODUCTION

Desalination is the process of purifying or reducing dissolved salts in seawater or in other words as a process for removing salt levels in water [1,2]. Seawater contains 3.5% salts, dissolved gases and substances, organic matter and insoluble particles [3]. The main salts found in seawater are chloride, sulfate, sodium, magnesium, calcium, potassium and the rest consists of bicarbonate, bromide, boric acid, strontium and fluoride. Desalination technology using membranes offers the latest options for achieving energy efficiency and cost-effectiveness of the desalination process. Developments in membrane technology including membrane advanced materials, module and process design, pretreatment and energy-saving have greatly reduced costs that have changed interest in commercial applications compared to other desalination processes.

Several desalination technologies include reverse osmosis, nanofiltration, electrodialysis, membrane distillation, membrane capacitive deionization and microbial desalination cell [4]. Among the liquid membranes that commonly used are supported liquid membrane (SLM), emulsion liquid membrane (ELM) and bulk liquid membrane (BLM). However, three of them still have some drawbacks, for example, BLM has a low surface area and mass transfer rate, ELM has emulsion damage problem while SLM has low stability [5]. To overcome this problem, Sugiura *et al*. [6] managed to get a stable membrane by trapping the liquid membrane into the cellulose acetate membrane coupled with a plasticizer that become a new generation of supported liquid membrane. This type of facilitated transport membrane is called a polymer inclusion membrane (PIM) possessing a very high stability [7]. Maryati [8] reported the salinity level of 96.696% decreased using Aliquat 336 single carrier compound, while 100% was achieved using Aliquat 336-TBP mixed carrier compounds.

Niama and Monir *et al*. [9] applied supported liquid and liquid emulsion membranes for desalination of seawater, but the results weren't encouranging enough due to lack of stability and requirement of emulsion stabilizing agent. Another research conducted by Djunaidi *et al*. [10] regarding the desalination of seawater using SLM succeeded in decreasing salinity levels up to 80% using D2EHPATBP and HTTA-TBP as synergetic carriers while using PIM with aliquat-TBP carriers also succeeded in reducing salinity levels in the same range with 25x dilution.

Thus, the desalination process with the right selection of carrier and system will lead to a greater extent of desalination. In this work, several polymer inclusion membranes were prepared

using different carriers *viz*., methyl trioctylammonium chloride (Aliquat 336), di-(2-ethylhexyl)phosphate (D2EHPA, 97%), thenoyl trifluoroacetone (HTTA, 99%), tributyl phosphate (TBP), eugenol p.a. (PE) in the presence of dibutyl ether (DBE) as plasticizer and PVC as base polymer for the desalination of seawater.

## EXPERIMENTAL

The chemicals *viz*. polyvinyl chloride, dibutyl ether, methyltrioctylammonium chloride (Aliquat 336), di-(2-ethylhexyl)-phosphate (D2EHPA, 97%), thenoyl trifluoroacetone (HTTA, 99%), tetrahydrofuran, tributyl phosphate (TBP), eugenol p.a. and $BF_3$-diethyl ether were purchased from Sigma-Aldrich, USA.

**Synthesis of polyeugenol (PE):** Eugenol (5 g) was added into a three-necked flask containing 1 mL of $BF_3$-diethyl ether. The mixture was stirred and again added 0.25 mL $BF_3$-diethyl ether after every 1 h. After 4 h of reaction, the polymerization was stopped by adding 1 mL of methanol. The formed gel was then dissolved with diethyl ether and washed thoroughly with distilled water until it reached neutral pH and finally dried over anhydrous $Na_2SO_4$. The gel was then dissolved with distilled water, dried and weighed.

**Preparation of PIM single carrier:** Polymer inclusion membrane (PIM) was prepared by mixing PVC (0.15 g) dissolved in 5 mL THF in 20 % single carrier solution *viz*. HTTA, D2EHPA, TBP, PE and aliquat 336 separately and 20% DBE as a plasticizer with continous stirring. After that the solution was poured in a petri dish and left for 24 h at room temperature, until transparent elastic membrane was formed.

**Preparation of 1:1 PIM mixed carriers:** PIM containing mixed carriers were also prepared in the same method as mentioned above. However, instead of single carrier, 20% mixed carrier solution *viz*. HTTA:TBP; D2EHPA:TBP; HTTA:Aliquat; D2EHPA:Aliquat in a ratio of 1:1 was used.

**Separation process (desalination):** The PIM membrane was placed between the feed phase as a source of analyte and the receiving phase as a source of separation. Feed phase consist of 1L seawater was collected from Marina Beach in Semarang, Indonesia, and the receiving phase was micro-filtered water. The transport desalination process was carried out by stirring each diffusion cell for 24 h at a constant speed.

**Salinity analysis:** Salinity meter (Kokido) was used for to measure the salinity in both feed and receiver phases. The Mg transport contents in the feed and receiver phases were also analyzed using AAS and the membrane surface morphology analysis was done using SEM.

## RESULTS AND DISCUSSION

**FTIR analysis:** The polymerization of eugenol produced a solid orange powder with a yield of 95.37% with a molecular weight of 6127.16 daltons (n = 37). Fig. 1 showed the absence of C=C group at 1648-1638 $cm^{-1}$ in the spectrum of eugenol and the disappearance of vinyl group at 997 and 915 $cm^{-1}$ indicates that the polymerization has successfully occured.

**SEM analysis:** The SEM analysis of blank PIM before transport at 2500x magnification in Fig. 2a shows a surface

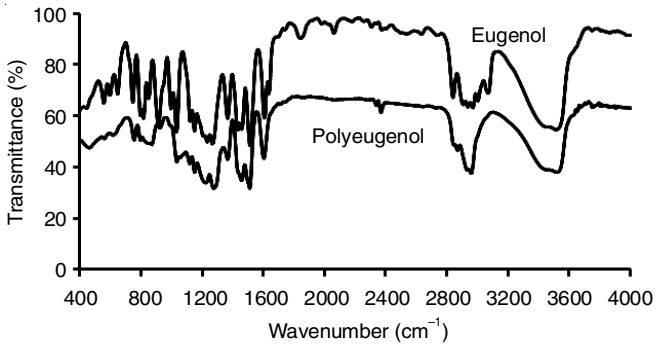


Fig. 1. FTIR spectra of eugenol and polyeugenol

morphology that tends to have no pores. Meanwhile, the PIM with different single carrier (Fig. 2b-d) gives a surface morphology that tends to form pores. Therefore, the presence of carriers was expected to optimize the value of salinity in the desalination process. The results of SEM analysis of PIM consisted of single carrier *viz*. HTTA and PE (Fig. 2e-f) showed that there were differences in surface morphology after the desalination, where the surface experienced buildup and blockage by white granules, which were possibly occured due to the salts received from the feed phase (seawater).

**Hydrophobicity of single carrier PIM:** Hydrophobic describes the interaction between the layer′s boundary of the solid and liquid phases [11]. Fig. 3 showed the successive hydrophobicity of a single carrier type PIM. By calculating the contact angle in hydrophobicity, each contact angle values obtained were 67.4º (polyeugenol), 66.3º (Aliquat-336)), 64.5º (blank), 82.06º (HTTA), 76.7º (TBP) and 86.4º (D2EHPA). Thus, HTTA and TBP membranes have greater hydrophobic properties due to its large contact angle values in contrast to other single carrier and the small contact angle value of blank, shows large hydrophilicity. The increasing hydrophilic nature possibly improves the desalination transport process or in other words, enables the ions to become more mobile during the desalination process. But in this case, desalination by PIM transportability is not only influenced by the membrane hydrophilicity but also by the type of carrier present.

**Salinity transport using single carrier:** The salinity transport process takes place through several stages. Initially saline spreads to the membrane feed phase interface, then binds to the carrier compound to form an ion pair. This process is continuous and reversible [12]. The salinity transport results (Fig. 4) showed that PIM membrane without a carrier (blank) is not able to carry out the desalination process optimally with salinity in the desalination process valued for 0 (no salinity transport), either from the feed phase or the receiving phase, which was caused by the absence of a carrier compound that would form ion pairs in blank membrane. In addition, it was also obtained that increasing the desalination transport process time will optimize the salinity value and the transport capacity of each carrier type, as seen from the salinity value exposure in the feed phase with an increase in time after 12 h.

Fig. 5 showed that HTTA, TBP and PE carriers have good salinity transport capabilities in the receiving phase after 24 h, which makes the carrier to pair with ions in the membrane

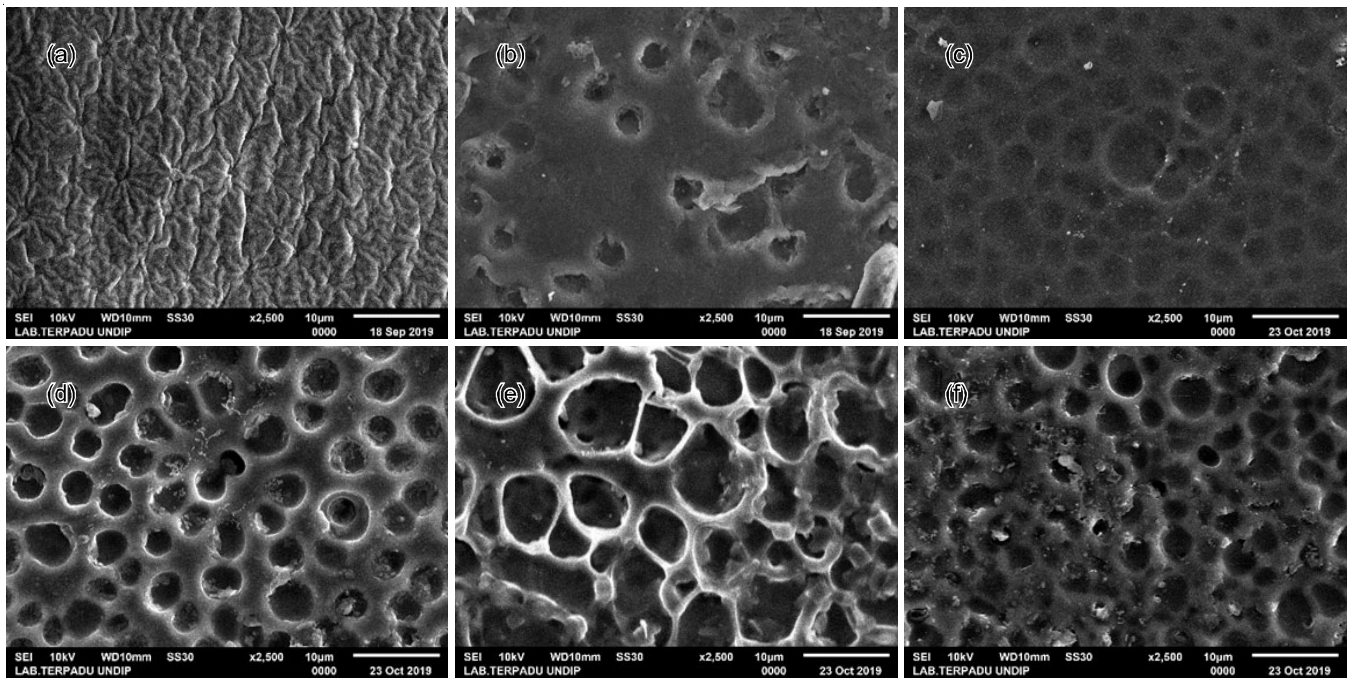


Fig. 2. SEM micrograph of polymer inclusion membrane using different carriers before and after transport

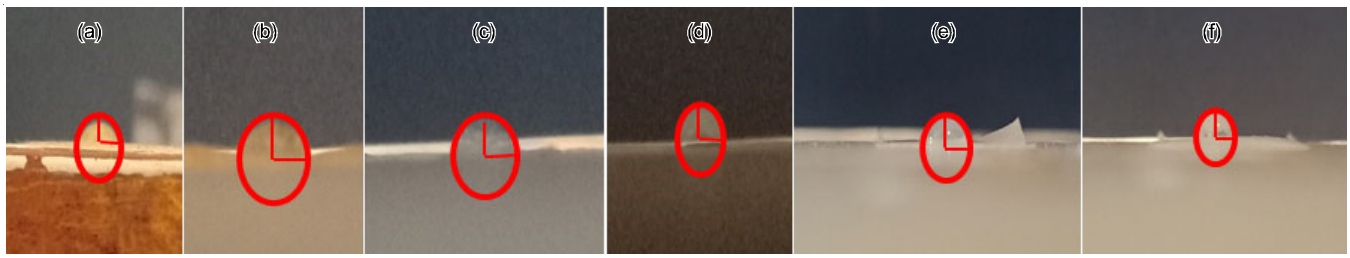


Fig. 3. Hydrophobicity of polymer inclusion membrane using single carrier a: polyeugenol; b: Aliquat-336; c: blank; d: HTTA; e: TBP and f: D2EHPA

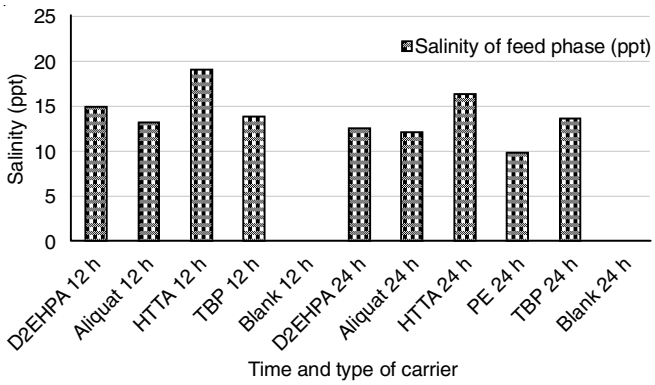


Fig. 4. Salinity of feed phase using different carriers in PIM after 12 and 24 h

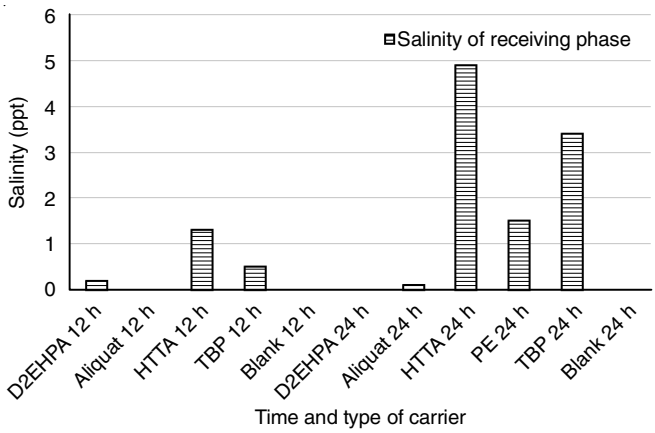


Fig. 5. Salinity of receiving phase using different carriers in PIM after 12 and 24 h

receptor phase interface. In the membrane receptor phase interface, the carrier and ion pair will be dissolved by carrier compound, HTTA, so that ions (anion or cation) will be released and exchanged with $OH^-$ in the receiving phase [12].

**Transport of magnesium using single carrier:** Fig. 6 shows Mg levels in both the feed phase and the receiver phase, where PE, HTTA and TBP carriers have a better tendency to transport magnesium ions as compared to other carriers, also represent the dual role of the carrier compound as well as the neutralization reaction resulted from the transfer of anions to the receiving phase [13]. Therefore, it showed that Mg cation present in the seawater was also transferred from the feed phase to the receiving phase in the process of seawater salinity transport. In this case, no leaching in the desalination transport process was observed.

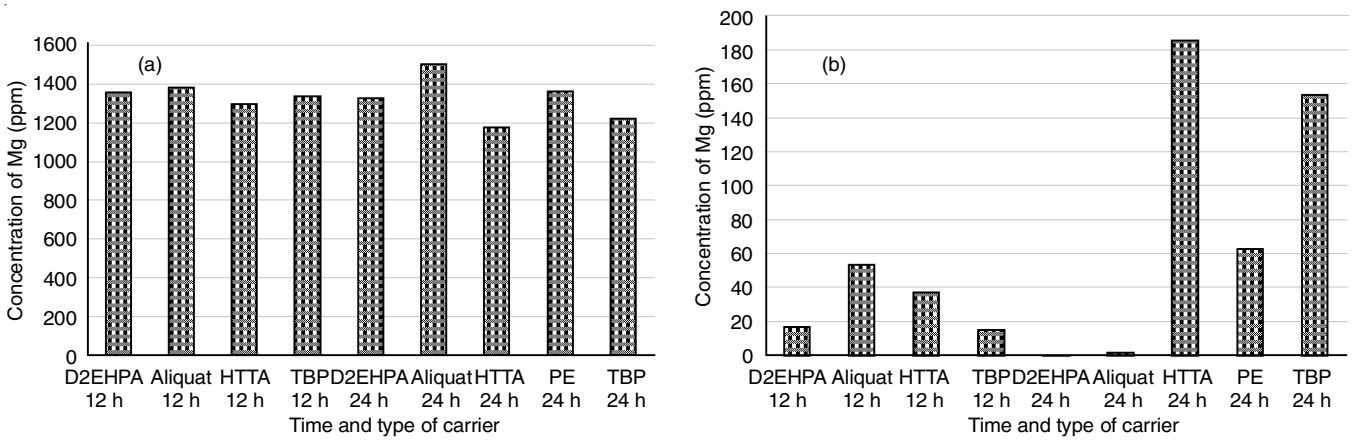


Fig. 6. Analysis of Mg level at feed phase (a) and receiving phase (b) using single carrier PIM

**Transport of magnesium ions using mixed carrier:** The amount of magnesium ion transported from the feed phase to the receiving phase is shown in Fig. 7. It is found that the feed phase and receiving phase in the presence of mixed carriers does not provide a significant magnesium transport value when compared with a single carrier, which is possible due to the fact that in the mixed carrier, the carrier and ion pair become difficult to spread on the membrane phase receptor interface. Thus, it can be concluded that the presence of a mixed carrier has no effect on Mg transport.

**Salinity transport by mixed carrier:** The salinity analysis (Fig. 8) showed that there was no significant difference in salinity values in the PIM of HTTA:TBP, D2EHPA:TBP, HTTA:aliquat and D2EHPA:aliquate mixed carriers. This might be due to the presence of mixed carrier makes it difficult for carrier with ions pairs to spread on the interface of the membrane receptor phase. So, it is concluded that using mixed carrier, the salinity transportability may be difficult to occur in the desali-nation transport process.

## Conclusion

Several polymer inclusion membranes containing either single or mixed carriers *viz*. dibutyl ether, methyl trioctyl-ammonium chloride (Aliquat 336), di-(2-ethylhexyl)phosphate (D2EHPA), thenoyl trifluoroacetone (HTTA), tributyl phosphate (TBP) and eugenol (PE) have been prepared. The large contact angle value using different carrier able to increase the hydro-phobic properties of PIM. It was found that polymer inclusion membrane with a mixed carriers does not give any significant salinity value in the desalination process.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

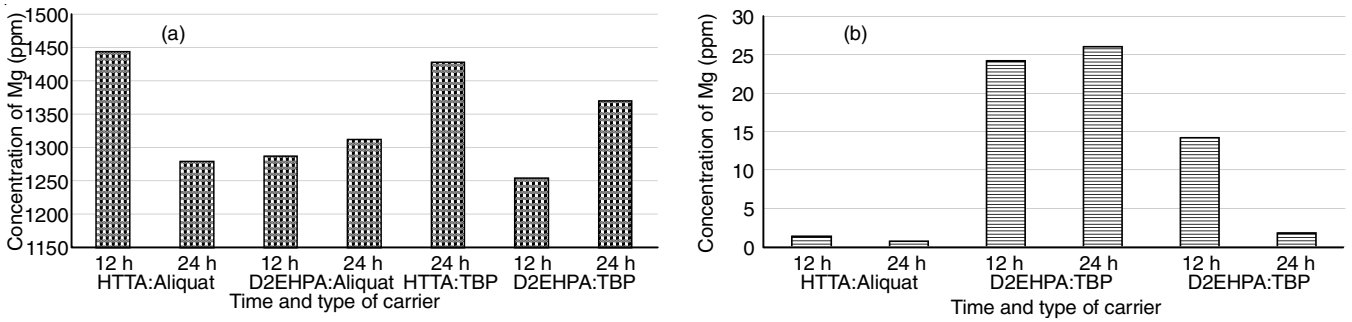


Fig. 7. Analysis of Mg level at feed phase (a) and receiving phase (b) using mixed carrier PIM

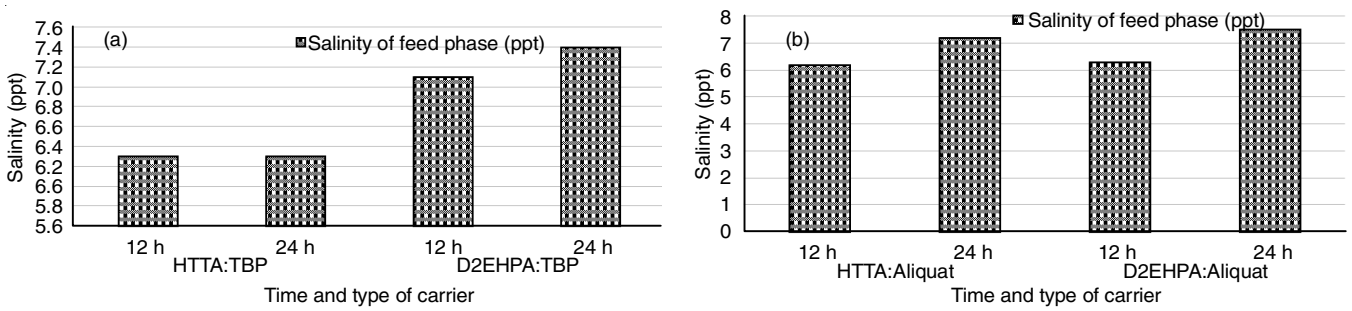


Fig. 8. Analysis of salinity using mixed carrier in PIM

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